

09/27/01

U.S. PTO

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(10/95)

U. S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

HUBR- 1195 (10107427)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/937810

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371INTERNATIONAL APPLICATION NO.
PCT/EP00/02251INTERNATIONAL FILING DATE
14 March 2000PRIORITY DATE CLAIMED
11 June 1999

TITLE OF INVENTION

COPOLYMERS BASED ON UNSATURATED MONO- OR DICARBOXYLIC ACID DERIVATIVES AND OXYALKYLENE GLYCOL ALKENYL ETHERS,
METHOD FOR THE PRODUCTION AND USE THEREOF

APPLICANT(S) FOR DO/EO/US

Gerhard ALBRECHT et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is the **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau.)
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:
17. ☐ The follow fees are submitted
18. ☒ Other: Form PTO 1449
Check for Filing Fee
Copy of Form PCT/PEA/409
Copy of Form PCT/RO/101

EXPRESS MAIL NO. EL 829764770 US MAILED September 27, 2001

09/937810

JC05 Rec'd PCT/PTO 2 7 SEP 2001

BASIC NATIONAL FEE (37 CFR 1.492(A)(1) - (5)):

Search Report has been prepared by the EPO or JPO \$860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) \$690.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ... \$710.00

Neither International preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1000.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	18 - 20 =	0	x \$78.00
Independent	1 - 3 =	0	x \$78.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$250.00

\$0

\$0

\$

TOTAL OF ABOVE CALCULATIONS = \$990

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

\$

SUBTOTAL =

\$

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

+

TOTAL NATIONAL FEE =

\$990

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property.

\$

TOTAL FEES ENCLOSED =

\$990

Amount to be:
refunded

\$

charged

\$

- a. ☒ A check in the amount of \$990.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 50-0624 in the amount of \$ 495 to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 50-0624. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Davir Rubin
FULBRIGHT & JAWORSKI L.L.P.
666 Fifth Avenue
New York, NY 10103
Customer No. 24972



SIGNATURE

David Rubin

September 27, 2001

NAME

40,314

REGISTRATION NUMBER

EXPRESS MAIL NO.EL 829764770 US mailed September 27, 2001

09/937810
JC05 Rec'd PCT/PTO 27 SEP 2001

CERTIFICATE OF EXPRESS MAIL

"Express Mail" mailing label # EL829764770 US

Date of Deposit September 27, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service on the date indicated above and is addressed to: Commissioner of Patents and Trademarks, Washington D.C. 20231

Fani Malikouzakis

(Name of Depositor)

Fani Malikouzakis 9/27/01

(Signature of Depositor)

Fulbright & Jaworski L.L.P.
666 Fifth Avenue
New York, New York 10103

HUBR 1195 - PFF/DR (10107427)

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<u>Pani Malikouzakis</u> (Name of Depositor)	
<u>Pani Malikouzakis</u> (Signature of Depositor)	

PATENT AND TRADEMARK IN THE UNITED STATES OFFICE

Applicants : Gerhard ALBRECHT et al.
Serial No. : To Be Assigned
Filed : Concurrently Herewith
For : COPOLYMERS BASED ON UNSATURATED MONO-
OR DICARBOXYLIC ACID DERIVATIVES AND
OXYALKYLENE GLYCOL ALKENYL ETHERS,
METHOD FOR THE PRODUCTION AND USE
THEREOF

September 27, 2001

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

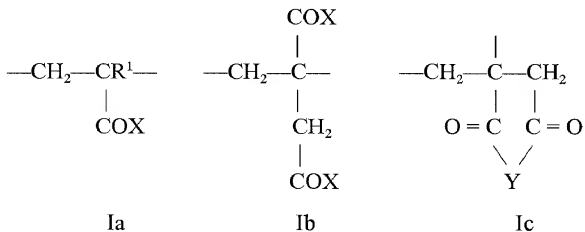
In advance of prosecution, please amend the above-identified patent application as follows:

IN THE CLAIMS:

Please cancel claims 1-18.

Please add the following new claims:

19. (New) A copolymer based on radicals of unsaturated monocarboxylic or dicarboxylic acid derivatives and oxyalkylene glycol alkenyl ethers, comprising
- a) from 51 to 95 mol% of structural units of the formula Ia and/or Ib and/or Ic



where

$R^1 =$ hydrogen or an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms,

$X =$ O_aM , $-O-(C_mH_{2m}O)_n-R^2$, $-NH-(C_mH_{2m}O)_n-R^2$,

$M =$ hydrogen, a monovalent or divalent metal cation, an ammonium ion or an organic amine radical,

$a =$ $\frac{1}{2}$ or 1,

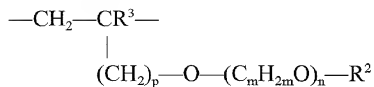
$R^2 =$ hydrogen, an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, a substituted or unsubstituted aryl radical having from 6 to 14 carbon atoms,

$Y =$ O, NR^2 ,

$m =$ 2 to 4 and

$n =$ 0 to 200,

- b) from 1 to 48.9 mol% of structural units of the general formula II



II

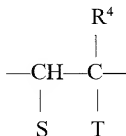
where

R^3 = is hydrogen or an aliphatic hydrocarbon radical having from 1 to 5 carbon atoms,

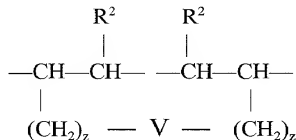
p is from 0 to 3,

and R^2 , m and n are as defined above,

- c) from 0.1 to 5 mol% of structural units of the formula selected from one of IIIa and IIIb



IIIa



IIIb

where

S = H, $\text{---COO}_a\text{M}$, ---COOR^5 ,

T = $\text{---U}^1\text{---(CH---CH}_2\text{---O)}_x\text{---(CH}_2\text{---CH}_2\text{O)}_y\text{---R}^6$



---W---R^7

$\text{---CO---[NH---(CH}_2\text{)}_3\text{]}_s\text{---W---R}^7$

$\text{---CO---O---(CH}_2\text{)}_z\text{---W---R}^7$

$\text{---(CH}_2\text{)}_z\text{---V---(CH}_2\text{)}_z\text{---CH=CH---R}^2$

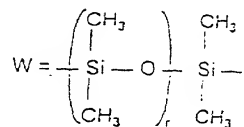
-COOR⁵ in the case of S = -COOR⁵ or

COO_nM

U¹ = -CO-NH-, -O-, -CH₂O-

U² = -NH-CO-, -O-, -OCH₂-

V = -O-CO-C₆H₄-CO-O- or -W-



R⁴ = H, CH₃,

R⁵ = an aliphatic hydrocarbon radical having from 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, an aryl radical having from 6 to 14 carbon atoms,

R⁶ = R², -CH₂-CH-U²-C=CH

$$\begin{array}{ccccc} & | & & | & | \\ & \text{R}^4 & & \text{R}^4 & \text{S} \end{array}$$

R⁷ = R², -[(CH₂)₃-NH]_s-CO-C=CH

$$\begin{array}{cc} & | & | \\ & \text{R}^4 & \text{S} \end{array}$$

-(CH₂)_z-O-CO-C=CH

$$\begin{array}{cc} & | & | \\ & \text{R}^4 & \text{S} \end{array}$$

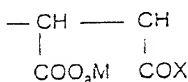
r = 2 to 100

s = 1, 2

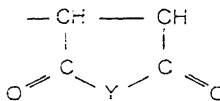
$$\begin{aligned}z &= 0 \text{ to } 4 \\x &= 1 \text{ to } 150 \\y &= 0 \text{ to } 15\end{aligned}$$

and

- d) from 0 to 47.9 mol of structural units of the general formula selected from one or both of IVa and IVb



IVa



IVb

where a, M, X and Y are as defined above.

20. (New) The copolymer according to claim 1, wherein R¹ is a methyl radical.
21. (New) The copolymer according to claim 1, wherein M is a monovalent or divalent metal cation selected from the group consisting of sodium, potassium, calcium and magnesium ions.
22. (New) The copolymer according to any of claim 1, wherein when R² = phenyl, the phenyl radical is substituted by one or more hydroxyl, carboxyl or sulfonic acid groups.
23. (New) The copolymer according to claim 1, wherein in formula II, p = 0 and m = 2.

24. (New) The copolymer according to claim 1, wherein it comprises from 55 to 75 mol% of structural units selected from one or more of formula Ia, Ib and Ic, from 19.5 to 39.5 mol% of structural units of the formula II, from 0.5 to 2 mol% of structural units selected from one or more of formula IIIa and IIIb and from 5 to 20 mol% of structural units selected from one or more of formula IVa and IVb.
25. (New) The copolymer according to claim 1, wherein it further comprises up to 50 mol% based on the sum of the structural units of the formulae I, II, III and IV, of structural units whose monomer is a vinyl or (meth)acrylic acid derivative.
26. (New) The copolymer according to claim 7, wherein the additional structural units are formed from a monomeric vinyl derivative styrene, α -methylstyrene, vinyl acetate, vinyl propionate, ethylene, propylene, isobutene, n-vinylpyrrolidone, allylsulfonic acid, methallylsulfonic acid, vinylsulfonic acid or vinylphosphonic acid.
27. (New) The copolymer according to claim 7, wherein the additional structural units are formed from a monomeric (meth)acrylic acid derivative hydroxyalkyl (meth)acrylate, acrylamide, methacrylamide, AMPS, methyl methacrylate, methyl acrylate, butyl acrylate or cyclohexyl acrylate.
28. (New) The copolymer according to any of claim 1, wherein it has a mean molecular weight of from 1000 to 100,000 g/mol.
29. (New) A process for preparing a copolymer according to claim 1, wherein from 51 to 95 mol% of an unsaturated monocarboxylic or dicarboxylic acid derivative, from 1 to 48.9 mol% of an oxyalkylene glycol alkenyl ether, from 0.1 to 5 mol%

of a vinylic polyalkylene glycol, polysiloxane or ester compound and from 0 to 55 mol% of a dicarboxylic acid derivative are polymerized with the aid of a free-radical initiator.

30. (New) The process according to claim 11, wherein from 55 to 75 mol% of an unsaturated monocarboxylic or dicarboxylic acid derivative, from 19.5 to 39.5 mol% of an oxyalkylene glycol alkenyl ether, from 0.5 to 2 mol% of a vinylic polyalkylene glycol, polysiloxane or ester compound and from 5 to 20 mol% of a dicarboxylic acid derivative are used.
31. (New) The process according to claim 11, wherein up to 50 mol%, in particular up to 20 mol%, based on the monomers comprising the structural units of the formulae I, II, III and IV, of a vinyl or (meth)acrylic acid derivative are additionally copolymerized.
32. (New) The process according to claim 11, wherein the polymerization is carried out in aqueous solution at a temperature of from 20 to 100°C.
33. (New) The process according to claim 14, wherein the concentration of the aqueous solution is from 30 to 50% by weight.
34. (New) The process according to claim 11, wherein the polymerization is carried out without solvents with the aid of a free-radical initiator at temperatures of from 20 to 150°C.
35. (New) Use of a copolymer according to claim 1 as an additive to aqueous suspensions based on mineral or bituminous binders.

36. (New) Use of the copolymer of claim 17, in an amount of from 0.01 to 10% by weight, based on the weight of the mineral binder.


REMARKS

An early and favorable response is earnestly solicited.

No fee is believed to be due, however, should a fee become due the Commissioner is hereby authorized to deduct any fee associated with this filing from Deposit Account No. 500624.

Respectfully submitted,

FULBRIGHT & JAWORSKI L.L.P.

By 
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WO 00/77058

PCT/EP00/02251

Copolymers based on unsaturated monocarboxylic or dicarboxylic acid derivatives and oxyalkylene glycol alkenyl ethers, process for producing them and their use

5

Description

10 The present invention relates to copolymers based on unsaturated monocarboxylic or dicarboxylic acid derivatives and oxyalkylene glycol alkenyl ethers, a process for preparing them and the use of these copolymers as additives for aqueous suspensions of inorganic or organic solids.

15 It is known that additives in the form of dispersants are often added to aqueous slurries of pulverulent inorganic or organic substances such as clays, porcelain slips, silicate flour, chalk, carbon black, ground rock, pigments, talc, polymer powders and
20 hydraulic binders for improving their processability, i.e. kneadability, spreadability, sprayability, pumpability or flow. These additives, which generally contain ionic groups, are able to break up agglomerates of solids, disperse the particles formed and in this
25 way improve the processability of, in particular, highly concentrated suspensions. This effect is also exploited in a targeted manner in the production of building material mixtures based on cement, lime and hydraulic binders based on calcium sulfate, optionally
30 in a mixture with organic (e.g. bituminous) components and also for ceramic compositions, refractory compositions and oilfield chemicals.

To convert these building material mixtures based on
35 the abovementioned binders into a ready-to-use, processable form, it is generally necessary to use significantly more make-up water than would be necessary for the subsequent hydration or curing

process. The voids formed in the component as a result of later evaporation of the excess water leads to significantly impaired mechanical strengths and stabilities.

5

To reduce this excess water content at a given processing consistency and/or to improve the processability at a given water/binder ratio, use is made of additives which are generally referred to as
10 water reduction agents or fluidizers. Known agents of this type are, in particular, polycondensation products based on naphthalenesulfonic or alkylnaphthalene-sulfonic acids (cf. EP-A-0 214 412) or melamine-formaldehyde resins containing sulfonic acid groups
15 (cf. DE-C 16 71 017).

A disadvantage of these additives is the fact that their excellent fluidizing action, especially in concrete construction, is maintained over only a short
20 period of time. The deterioration in the processability of concrete mixtures ("slump loss") in a short time can lead to problems especially where there is a long period of time between make-up and installation of the fresh concrete, for example as a result of long
25 conveyance and transport paths.

An additional problem arises when such fluidizers are employed in mining and in interior applications (drying of cardboard-faced plasterboard, anhydrite screed
30 applications, manufacture of finished concrete components), since release of the toxic formaldehyde present in the products as a result of the manufacturing method can occur and thus lead to considerable occupational hygiene problems. For this
35 reason, attempts have already been made to develop formaldehyde-free concrete fluidizers based on maleic monoesters and styrene, for example as described in EP-A-0 306 449. The flow of concrete mixtures can be

maintained over a sufficiently long period of time by means of these additives, but the original, very high dispersant action is lost very quickly after storage of the aqueous fluidizer formulation as a result of hydrolysis of the polymeric ester.

This problem does not occur in the case of fluidizers based on alkylpolyethylene glycol allyl ethers and maleic anhydride as described in EP-A-0 373 621. However, these products are, like those described above, surface-active compounds which introduce undesirably high proportions of air pores into the concrete mixture, resulting in deterioration in the finished state [sic] and stability of the cured building material.

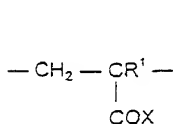
For this reason it is necessary to add antifoams such as tributyl phosphate, silicone derivatives and various water-insoluble alcohols in concentrations of from 0.1 to 2% by weight, based on the solids content, to the aqueous solutions of these polymeric compounds. Mixing-in these antifoam components and maintaining a storage-stable homogeneous form of the corresponding formulations is very difficult even when these antifoams are added in the form of emulsions.

The problem of demixing can be solved by complete or at least partial incorporation of a foam-inhibiting or air-repellant structural unit into the copolymer, as described in DE 195 13 126 A1.

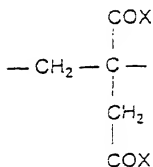
However, it has been found that the high effectiveness and the low "slump loss" of the copolymers described here often leads to unsatisfactory 24-hour strengths of the concrete. Furthermore, such copolymers do not have optimum properties, especially where a particularly dense and therefore high-strength and high-stability concrete is to be produced using the lowest possible

proportion of water and steam curing (finished parts industry) for accelerating the curing process is to be dispensed with.

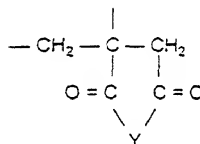
- 5 It is therefore an object of the invention to provide new copolymers which do not have the abovementioned disadvantages of the known agents, i.e. which maintain the processability of highly concentrated building material mixtures for an appropriate length of time
- 10 even in small amounts and at the same time give an increased strength in the cured state of the building material due to a drastic decrease in the water/binder ratio.
- 15 This object is achieved according to the invention by copolymers based on radicals of unsaturated mono-carboxylic or dicarboxylic acid derivatives and oxyalkylene glycol alkenyl ethers, which are characterized in that they comprise
- 20 a) from 51 to 95 mol% of structural units of the formula Ia and/or Ib and/or Ic



Ia



Ib



Ic

25

where R^1 = hydrogen or an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms,

$X = O_aM, -O-(C_mH_{2m}O)_n-R^2, -NH-(C_mH_{2m}O)_n-R^2,$

30

$M =$ hydrogen, a monovalent or divalent metal cation, an ammonium ion or an organic amine radical,

a = $\frac{1}{2}$ or 1,

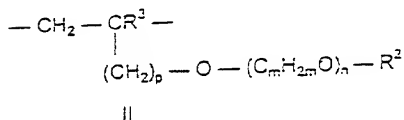
R^2 = hydrogen, an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, a substituted or unsubstituted aryl radical having from 6 to 14 carbon atoms,

Y = O, NR^2 ,

m = 2 to 4 and

n = 0 to 200,

b) from 1 to 48.9 mol% of structural units of the general formula II



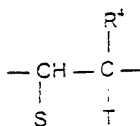
where

R^3 is hydrogen or an aliphatic hydrocarbon radical having from 1 to 5 carbon atoms,

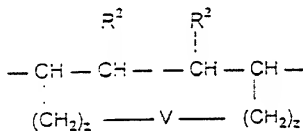
p is from 0 to 3

and R^2 , m and n are as defined above,

c) from 0.1 to 5 mol% of structural units of the formula IIIa or IIIb

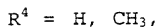
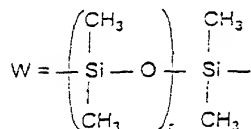
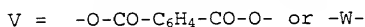
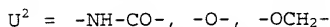
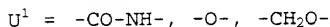
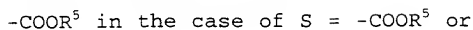
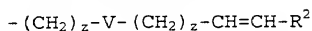
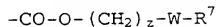
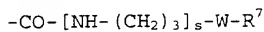
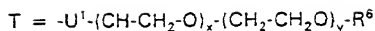
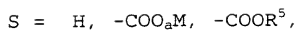


IIIa

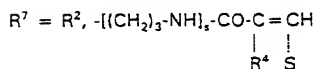
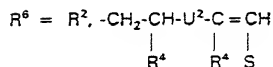


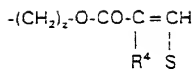
IIIb

where



R^5 = an aliphatic hydrocarbon radical having from 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, an aryl radical having from 6 to 14 carbon atoms,





$$r = 2 \text{ to } 100$$

$$s = 1, 2$$

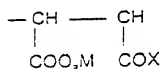
$$z = 0 \text{ to } 4$$

$$x = 1 \text{ to } 150$$

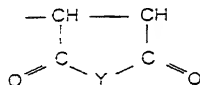
$$y = 0 \text{ to } 15$$

and

- d) from 0 to 47.9 mol [lacuna] of structural units of the general formula IVa and/or IVb



IVa



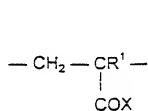
IVb

where a, M, X and Y are as defined above.

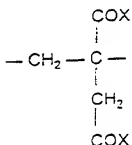
It has surprisingly been found that very small amounts of the copolymers of the invention based on unsaturated monocarboxylic or dicarboxylic acid derivatives and oxyalkylene glycol alkenyl ethers added to aqueous building material suspensions give the suspensions excellent processing properties without delaying strength development. It was particularly surprising that a drastic decrease in the water/binder ratio still leads to highly fluid building materials when the copolymers of the invention are added and no segregation of individual constituents of the building material mixture occurs.

The copolymers of the invention comprise at least three, but preferably four, structural units a), b), c) and d). The first structural unit a) is a

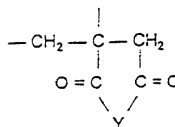
monocarboxylic or dicarboxylic acid derivative having the general formula Ia, Ib or Ic.



Ia



Ib



Ic

5 In the case of the monocarboxylic acid derivative Ia, R¹ is hydrogen or an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, preferably a methyl group. X in the structures Ia and Ib is -O_aM and/or
10 -O-(C_mH_{2m}O)_n-R² or -NH-(C_mH_{2m}O)_n-R², where M, a, m, n and R² are defined as follows:

M is hydrogen, a monovalent or divalent metal cation, ammonium, an organic amine radical, and a = ½ or 1
15 depending on whether M is a monovalent or divalent cation. Organic amine radicals are preferably substituted ammonium groups derived from primary, secondary or tertiary C₁₋₂₀-alkylamines, C₁₋₂₀-
20 alkanolamines, C₅₋₈-cycloalkylamines and C₈₋₁₄-arylamines. Examples of suitable amines from which these radicals are derived are methylamine, dimethylamine, trimethylamine, ethanolamine, diethanolamine, triethanolamine, methyldiethanolamine, cyclohexylamine, dicyclohexylamine, phenylamine,
25 diphenylamine in the protonated (ammonium) form.

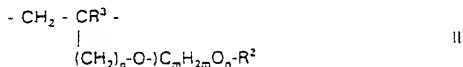
R² can be hydrogen, an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, an
30 aryl radical having from 6 to 14 carbon atoms which may also be substituted, m = 2 to 4 and n = 0 to 200. The aliphatic hydrocarbon radicals can be linear or branched and saturated or unsaturated. Preferred

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cycloalkyl radicals are cyclopentyl or cyclohexyl radicals, preferred aryl radicals are phenyl or naphthyl radicals which may also be substituted by groups such as -CN, -COOR¹, -R¹, -OR¹ and preferably by
 5 hydroxyl, carboxyl or sulfonic acid groups.

In place of or in addition to the dicarboxylic acid derivative of the formula Ib, the structural unit a) (monocarboxylic or dicarboxylic acid derivative) can
 10 also be present in cyclic form corresponding to formula Ic, where Y = O (acid anhydride) or NR² (acid imide) with the above-described meanings for R².

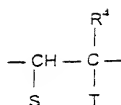
The second structural unit b) corresponds to formula II
 15



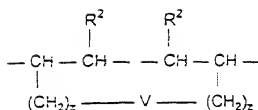
and is derived from oxyalkylene glycol alkenyl ethers. m, n and R² are as defined above. R³ is hydrogen or an
 20 aliphatic hydrocarbon radical having from 1 to 5 carbon atoms which may be linear or branched or saturated or unsaturated. p can be from 0 to 3.

In the formulae Ia, Ib and II, m is preferably 2 and/or
 25 3 so that the structural units are polyalkylene oxide groups derived from polyethylene oxide and/or polypropylene oxide. In a further preferred embodiment, p in formula II is 0 or 1, i.e. the structural units are vinyl and/or alkyl polyalkoxylates.

30 The third structural unit c) corresponds to the formula IIIa or IIIb



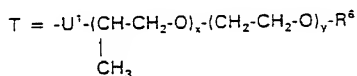
IIIa



IIIb

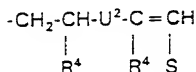
In the formula IIIa, R⁴ can be H or CH₃ depending on whether the structural units are acrylic or methacrylic acid derivatives. S can be -H, -COO_aM or -COOR⁵, where a and M are as defined above and R⁵ is an aliphatic hydrocarbon radical having from 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms or an aryl radical having from 6 to 14 carbon atoms. The aliphatic hydrocarbon radical can be linear or branched, saturated or unsaturated. Preferred cycloaliphatic hydrocarbon radicals are cyclopentyl or cyclohexyl radicals; preferred aryl radicals are phenyl or naphthyl radicals. In the case of T = -COOR⁵, S = COO_aM or -COOR⁵. When both T and S are COOR⁵, the corresponding structural units are derived from dicarboxylic esters.

Apart from these ester groups, the structural units c) may also comprise other hydrophobic structural elements. These include polypropylene oxide or polypropylene oxide-polyethylene oxide derivatives of the formula



x is from 1 to 150 and y is from 0 to 15. The polypropylene oxide(polyethylene oxide) derivatives can be linked via a group U¹ to the ethyl radical of the structural unit c) corresponding to the formula IIIa, where U¹ = -CO-NH-, -O- or -CH₂-O. The structural unit is thus the amide, vinyl ether or allyl ether

corresponding to the structural unit of the formula IIIa. R⁶ may in turn be as defined for R² (see above) or be



5

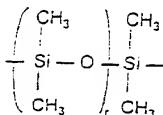
where U² = -NH-CO-, -O- or -OCH₂-, and S is as defined above. These compounds are polypropylene oxide(-polyethylene oxide) derivatives of the bifunctional alkenyl compounds corresponding to the formula IIIa.

10

As a further hydrophobic structural element, the compounds of the formula IIIa may contain polydimethylsiloxane groups, which in the formula IIIa corresponds to T = -W-R⁷.

15

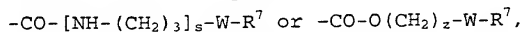
W is



20

(hereinafter referred to as a polydimethylsiloxane group), R⁷ can be as defined for R² and r can be from 2 to 100.

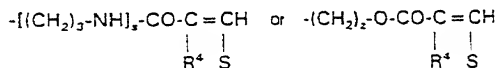
The polydimethylsiloxane group can not only be bound directly to the ethylene radical of the formula IIIa, but also via the group



where R⁷ is preferably as defined for R² and s = 1 or 2

and z = 0 to 2. R⁷ may also be a radical of the formula

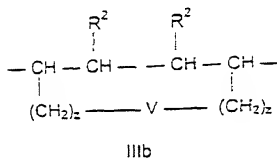
30



The compounds are then bifunctional ethylene compounds of the formula IIIa which are linked to one another via the respective amide or ester groups, with only one ethylene group having been copolymerized.

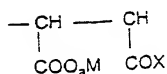
A similar situation applies to the compounds of the formula IIIa, in which $T = (CH_2)_z - V - (CH_2)_z - CH=CH - R^2$, where $z = 0$ to 4 , V is either a polydimethylsiloxane radical W or a $-O-CO-C_6H_4-CO-O-$ radical and R^2 is as defined above. These compounds are derived from the corresponding dialkylphenyldicarboxylic esters or dialkylpolydimethylsiloxane derivatives.

Within the scope of the present invention, it is also possible for not only one but also both ethylene groups of the bifunctional ethylene compounds to be copolymerized. This gives structural units corresponding to the formula IIIb

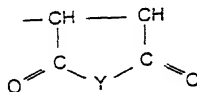


where R^2 , V and z are as defined above.

The fourth structural unit d) is derived from an unsaturated dicarboxylic acid derivative and has the formula IVa and/or IVb



IVa



IVb

where a, M, X and Y are as defined above.

According to the invention, the copolymers of the invention comprise from 51 to 95 mol% of structural units of the formula Ia and/or Ib and/or Ic, from 1 to 48.9 mol% of structural units of the formula II, from 0.1 to 5 mol% of structural units of the formula IIIa and/or IIIb and from 0 to 47.9 mol% of structural units of the formula IVa and/or IVb.

Preference is given to copolymers comprising from 55 to 75 mol% of structural units of the formula Ia and/or Ib, from 19.5 to 39.5 mol% of structural units of the formula II, from 0.5 to 2 mol% of structural units of the formula IIIa and/or IIIb and from 5 to 20 mol% of structural units of the formula IVa and/or IVb.

In a preferred embodiment, the copolymers of the invention further comprise up to 50 mol%, in particular up to 20 mol%, based on the sum of the structural units a to d, of structures which are derived from monomers based on vinyl or (meth)acrylic acid derivatives such as styrene, α -methylstyrene, vinyl acetate, vinyl propionate, ethylene, propylene, isobutene, hydroxyalkyl (meth)acrylates, acrylamide, methacrylamide, N-vinylpyrrolidone, allylsulfonic acid, methallylsulfonic acid, vinylsulfonic acid, vinylphosphonic acid, AMPS, methyl methacrylate, methyl acrylate, butyl acrylate, allylhexyl acrylate, etc.

The number of repeating structural units in the copolymers is not subject to any restrictions. However, copolymers having mean molecular weights of from 1000 to 100,000 g/mol have been found to be particularly advantageous.

The copolymers of the invention can be prepared in various ways. The important thing is that from 51 to

95 mol% of an unsaturated monocarboxylic or dicarboxylic acid derivative, from 1 to 48.9 mol% of an oxyalkylene alkenyl ether, from 0.1 to 5 mol% of a vinylic polyalkylene glycol, polysiloxane or ester
5 compound and from 0 to 55 mol% of a dicarboxylic acid derivative are polymerized by means of a free-radical initiator.

As unsaturated monocarboxylic or dicarboxylic acid derivatives which form the structural units of the formula Ia, Ib or Ic, preference is given to using: acrylic acid, methacrylic acid, itaconic acid, itaconic anhydride, itaconimide and the monoamide of itaconic acid.
10

In place of acrylic acid, methacrylic acid, itaconic acid and the monoamide of itaconic acid, it is also possible to use monovalent or divalent metal salts, preferably sodium, potassium, calcium or ammonium salts.
15
20

If the acrylic, methacrylic or itaconic acid derivative is an ester, preference is given to using derivatives whose alcoholic component is a polyalkylene glycol of the general formula $\text{HO}-(\text{C}_m\text{H}_{2m}\text{O})_n-\text{R}_2$, where $\text{R}^2 = \text{H}$, an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, a substituted or unsubstituted aryl radical having from 6 to 14 carbon
25
30 atoms and $m = 2$ to 4 and $n = 0$ to 200.

Preferred substituents on the aryl radical are $-\text{OH}-$, $-\text{COO}^\ominus$ or $-\text{SO}_3^\ominus$ groups.

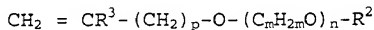
35 The unsaturated monocarboxylic acid derivatives can be present only as monoesters, while in the case of the dicarboxylic acid itaconic acid, diester derivatives are also possible.

The derivatives of the formulae Ia, Ib and Ic can also be present as mixtures of esterified and free acids and are preferably used in an amount of from 55 to 75 mol%.

5

The second component used according to the invention for preparing the copolymers of the invention is an oxyalkylene glycol alkenyl ether which is preferably used in an amount of from 19.5 to 39.5 mol%. Preferred oxyalkylene glycol alkenyl ethers correspond to the formula V

10



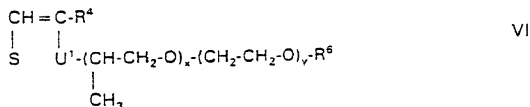
15

where $\text{R}^3 = \text{H}$ or an aliphatic hydrocarbon radical having from 1 to 5 carbon atoms and $p = 0$ to 3. R^2 , m and n are as defined above. The use of polyethylene glycol monovinyl ethers ($p = 0$ and $m = 2$) has been found to be particularly advantageous, with n preferably being from 1 to 50.

20

As third component used according to the invention for introducing the structural unit c), preference is given to using from 0.5 to 2 mol% of a vinylic polyalkylene glycol, polysiloxane or ester compound. Preferred vinylic polyalkylene glycol compounds are derivatives having the formula VI,

25

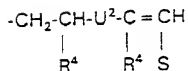


30

where S is $-\text{H}$ or COO_aM and U^1 is $-\text{CO}-\text{NH}-$, $-\text{O}-$ or $-\text{CH}_2\text{O}-$, i.e. the vinylic polyalkylene glycol compounds are the acid amide, vinyl or allyl ethers of the corresponding polypropylene glycol or polypropylene glycol-polyethylene glycol derivatives. x can be from 1 to 150

35

and y can be from 0 to 15. R^6 can either be as defined for R^1 or be



5

where $U^2 = \text{-NH-CO-}$, -O- or $\text{-OCH}_2\text{-}$ and $S = \text{-COO}_a\text{M}$ and preferably -H .

10 In the case of $R^6 = R^2$ and R^2 preferably being H, the compounds are the polypropylene glycol(-polyethylene glycol) monoamides or ethers of the corresponding acrylic ($S = \text{H}$, $R^4 = \text{H}$), methacrylic ($S = \text{H}$, $R^4 = \text{CH}_3$) or maleic ($S = \text{COO}_a\text{M}$ - $R^4 = \text{H}$) acid derivatives. Examples of such monomers are the N-(methyl-

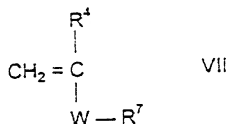
15 polypropylene glycol)monoamide of maleic acid, the N-(methoxy-polypropylene glycol-polyethylene glycol)-monoamide of maleic acid, polypropylene glycol vinyl ether and polypropylene glycol allyl ether.

20 In the case of $R^6 \neq R^2$, the compounds are bifunctional vinyl compounds whose polypropylene glycol(-polyethylene glycol) derivatives are joined to one another via amide or ether groups (-O- or $\text{-OCH}_2\text{-}$). Examples of such compounds are polypropylene glycol bismaleamide,

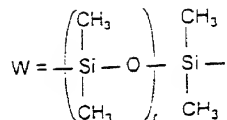
25 polypropylene glycol diacrylamide, polypropylene glycol dimethacrylamide, polypropylene glycol divinyl ether, polypropylene glycol diallyl ether.

As vinylic polysiloxane compound, preference is given

30 to derivatives corresponding to the formula VII,



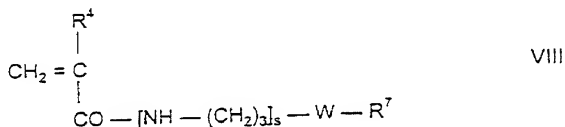
where $R^4 = -H$ or CH_3 ,



5 and $r = 2$ to 100 and $R^7 = R^2$. Examples of such monomers are monovinylpolydimethylsiloxane.

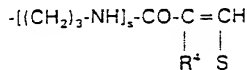
Further vinylic polysiloxane compounds which can be used are derivatives of the formula VIII,

10



where $s = 1$ or 2, R^4 and W are as defined above and R^7 can either be as defined for R^2 or be

15

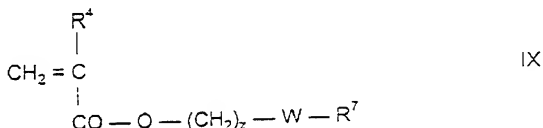


and S is as defined above and is preferably hydrogen or $-COOR^5$.

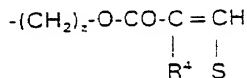
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Examples of such monomers having a vinyl function ($R^7 = R^2$) are polydimethylsiloxanepropylmaleamide or polydimethylsiloxanedipropyleneaminomaleamide. In the case of $R^7 \neq R^2$, the compounds are divinyl compounds
25 such as polydimethylsiloxanebis(propylmaleamide) or polydimethylsiloxanebis(dipropyleneaminomaleamide).

As further vinylic polysiloxane compound, preference is given to using a derivative corresponding to the formula IX:



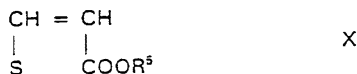
where z is from 0 to 4 and R^4 and W are as defined above. R^7 can either be as defined for R^2 or be



where S is as defined above and is preferably hydrogen. Examples of such monovinylic compounds ($\text{R}^7 = \text{R}^1$) are polydimethylsiloxane(1-propyl 3-acrylate) or polydimethylsiloxane(1-propyl 3-methacrylate).

In the case of $\text{R}^7 \neq \text{R}^2$, the compounds are divinyl compounds such as polydimethylsiloxanebis(1-propyl 3-acrylate) or polydimethylsiloxanebis(1-propyl 3-methacrylate).

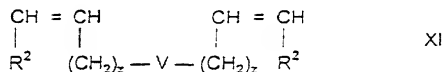
Vinylic ester compounds used for the purposes of the present invention are preferably derivatives of the formula X,



where $\text{S} = \text{COO}_2\text{M}$ or $-\text{COOR}^5$ and R^5 is an aliphatic hydrocarbon radical having from 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms or an aryl radical having from 6 to 14

carbon atoms. a and M are as defined above. Examples of such ester compounds are di-n-butyl maleate or fumarate or mono-n-butyl maleate or fumarate.

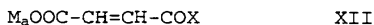
- 5 Furthermore, it is also possible to use compounds of the formula XI



- 10 where z is from 0 to 4 and R^2 is as defined above. V can also be as defined for W (i.e. a polydimethylsiloxane group), which corresponds to a dialkenylpolydimethylsiloxane compound such as divinylpolydimethylsiloxane. Alternatively, V can also be
 15 $-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-$. These compounds are dialkenyl phthalic acid derivatives. A typical example of such a phthalic acid derivative is diallyl phthalate.

- The molecular weights of the compounds which form the
 20 structural unit c) can be varied within wide limits and are preferably in the range from 150 to 10,000.

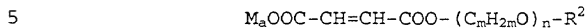
- As fourth component for preparing the copolymers of the invention, preference is given to using from 5 to
 25 20 mol% of an unsaturated dicarboxylic acid derivative of the formula XIII:



- 30 where a, M and X are as defined above.

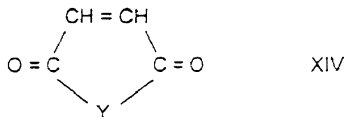
- When $\text{X} = \text{OM}_a$, the unsaturated dicarboxylic acid derivative is derived from maleic acid, fumaric acid, monovalent or divalent metal salts of these
 35 dicarboxylic acids, e.g. the sodium, potassium, calcium or ammonium salt or salts with an organic amine

radical. Monomers which form the unit Ia can further comprise polyalkylene glycol monoesters of the abovementioned acids having the general formula XIII:



where a, m, n and R^2 are as defined above.

10 The fourth component can be derived from unsaturated dicarboxylic anhydrides and imides of the general formula XIV (5 to 20 mol%)



15 where Y is as defined above.

In a preferred embodiment of the invention, further monomers as described above can be used in amounts of up to 50 mol%, preferably up to 20 mol%, based on the sum of the structural units a) to d).

25 The copolymers of the invention can be prepared by the customary copolymerization methods. A particular advantage is that, according to the invention, the copolymerization can be carried out without solvents or else in aqueous solution. In both cases, the reactions are carried out under atmospheric pressure and therefore do not pose a safety problem.

30 If the process is carried out in aqueous solution, the polymerization is carried out at from 20 to 100°C with the aid of a customary free-radical initiator, with the concentration of the aqueous solution preferably being set to from 30 to 50% by weight. In a preferred
35 embodiment, the free-radical polymerization is carried

out in the acid pH range, in particular at a pH of from 4.0 to 6.5, with conventional initiators such as H_2O_2 being able to be used without there being a risk of ether cleavage, as a result of which the yields would be greatly reduced.

In the process of the invention, preference is given to placing the unsaturated dicarboxylic acid derivative which forms the structural unit d) in partially neutralized form in aqueous solution, preferably together with the polymerization initiator, in a reaction vessel and introducing the remaining monomers as soon as the initial charge has reached the required reaction temperature. Polymerization aids which reduce the activation threshold of the preferably peroxidic initiator can be added separately, so that the copolymerization can occur at relatively low temperatures. In a further, preferred embodiment, the unsaturated dicarboxylic acid derivative and also the free-radical initiator are metered into the initial charge in the reactor in separate streams or in a common stream. This provides an ideal solution to the problem of heat removal.

However, it is also possible to place the polyoxyalkylene glycol alkenyl ethers which form the structural unit b) in the reaction vessel and to introduce the monocarboxylic or dicarboxylic acid derivative (structural unit a)) in such a way that a uniform distribution of the monomer units over the polymer chain is achieved.

The type of polymerization initiators, polymerization activators and other auxiliaries, e.g. molecular weight regulators, used is not critical. Initiators which can be used are the customary free-radical formers such as hydrogen peroxide, sodium, potassium or ammonium peroxodisulfate, tert-butyl hydroperoxide, dibenzoyl

peroxide, sodium peroxide, 2,2'-azobis(2-amidinopropane) dihydrochloride, azobisisobutyronitrile, etc. If redox systems are used, it is, for example, possible to combine the above-mentioned

5 initiators with activators having a reducing action. Examples of such reducing agents are Fe(II) salts, sodium hydroxymethanesulfinate dihydrate, alkali metal sulfites and metabisulfites, sodium hypophosphite, hydroxylamine hydrochloride, thiourea, etc.

10 A particular advantage of the copolymers of the invention is that they can also be prepared without solvents, which can be achieved with the aid of customary free-radical initiators at temperatures of

15 from 60 to 150°C. This variant is particularly advantageous for economic reasons when the copolymers of the invention are to be used directly in water-free form, because costly removal of the solvent, in particular water (for example by spray drying), then

20 becomes unnecessary.

The copolymers of the invention are very useful as additives for aqueous suspensions of inorganic and organic solids, in particular those based on mineral or

25 bituminous binders such as cement, plaster of Paris, lime, anhydrite or other building materials based on calcium sulfate, or based on pulverulent dispersion binders which are advantageously used in an amount of from 0.01 to 10% by weight, in particular from 0.05 to

30 5% by weight, based on the weight of the mineral binder. However, the copolymers of the invention can also be used very successfully in the fields of ceramic compositions, refractory compositions and oilfield chemicals.

35 The following examples illustrate the invention.

ExamplesExample 1

5 3300 g (3.00 mol) of methylpolyethylene glycol 1100 monovinyl ether (mean molecular weight: 1100 g/mol) were placed as a melt at 50°C in a 10 l double-walled reaction vessel provided with thermometer, stirrer, reflux condenser and two inlets for separate feed
10 streams. 3200 g of tap water were added, giving a strongly alkaline aqueous solution of the vinyl ether. While stirring and cooling, 58.80 g (0.60 mol) of maleic anhydride dissolved in 137.20 g of water (corresponding to a 30% strength solution) and,
15 separately, 10.86 g of 20% strength aqueous sodium hydroxide were added, with the temperature being kept below 30°C.

33.00 g (0.0165 mol) of a reaction product of a
20 butanol-initiated bifunctional NH₂-terminated ethylene oxide-propylene oxide block polymer (EO 4, PO 27; molecular weight: 1800 g) with maleic anhydride were subsequently added with brief intensive stirring, and 930 mg of FeSO₄·7H₂O, 5.97 g of 3-mercaptopropionic acid
25 and 34.40 g of 50% strength aqueous hydrogen peroxide were added in succession. At a temperature of 30°C, 281.00 g (3.90 mol) of acrylic acid dissolved in 843 g of tap water (25% strength solution) comprising an additional 17.90 g of 3-mercaptopropionic acid as
30 regulator were subsequently added to the initial charge over a period of 75 minutes. 252 ml of a 2% strength aqueous solution of sodium hydroxymethanesulfinate dihydrate were metered in separately over a period of 97 minutes, with the temperature rising to a maximum of
35 35.8°C.

After the addition was complete, the mixture was stirred for another 15 minutes at 30°C and brought to a

pH of 6.50 by addition of 801.70 g of 20% strength aqueous sodium hydroxide. The yellowish, turbid aqueous composition contained 41.6% by weight of solids. The weight average molecular weight of the copolymer was 35,350 g/mol; yield: 9220 g.

Example 2

The procedure of Example 1 was repeated, but a vinyl ether having a mean molecular weight of 2000 g/mol was used in place of the vinyl ether (MW = 1100) used in Example 1.

The following amounts of the structure-forming components were used:

205.60 g (2.853 mol)	of acrylic acid
3156.80 g (1.5784 mol)	of methylpolyethylene glycol 2000 monovinyl ether
47.35 g (0.025 mol)	of poly(PO-block-EO)maleamide (MW: 1900 g/mol)
92.80 g (0.946 mol)	of maleic anhydride

8705.2 g of a turbid, yellowish product having a solids content of 42.0% by weight were obtained. The weight average molecular weight was 32,150 g/mol.

Example 3

Example 1 was repeated, but 218.40 g (1.95 mol) of itaconic anhydride as a 25% strength aqueous solution were used as feed stream 1 in place of the acrylic acid used in Example 1. The aqueous copolymer obtained after neutralization with aqueous sodium hydroxide (25%) had a weight average molecular weight of 25,400 g/mol (solids content: 43.0% by weight).

Example 4

The procedure of Example 1 was repeated, with the following changes being made:

5

In addition to the initially charged

58.80 g (0.60 mol) of maleic anhydride

3300.00 g (3.00 mol) of methylpolyethylene glycol
1100 monovinyl ether

10 33.00 g (0.0165 mol) of poly(EO-block-PO)maleamide,
an addition of

175.00 g (0.50 mol) of a methylpolyethylene glycol
methacrylate (MW = 350 g/mol)

was made to the initial charge.

15

The proportion of acrylic acid in feed stream 1
remained unchanged (3.90 mol). As in Example 1, a
yellowish, turbid storage-stable aqueous suspension
having a solids content of 42.7% by weight
20 (M = 39,900 g/mol, yield: 9402 g).

Example 5

A copolymer of

25

1.37 mol of methacrylic acid (feed stream)

0.68 mol of ethylene glycol monovinyl ether
(initial charge)

0.005 mol of poly(EO₄-block-PO₂₇)maleic monoamide
30 (initial charge)

0.55 mol of methylpolyethylene glycol 1100
monomaleate (initial charge)

0.10 mol of maleic anhydride (feed stream)

35 was prepared as described in Example 1, but with a 25%
strength aqueous solution of methacrylic acid being
added instead of acrylic acid. Furthermore, an
additional feed stream consisting of a 25% strength

solution of maleic anhydride in water was used. In addition, methylpolyethylene glycol 1100 monomaleate was used in the initial charge.

- 5 The white aqueous turbid end product obtained had a polymer content of 43.7% by weight at a mean molecular weight of 36,500 g/mol.

Example 6

10

Example 1 was repeated, but 78.00 g (0.75 mol) of styrene were additionally dispersed in the initial charge. The odorless end product had a light yellow color (solids content: 42.0% by weight; MW = 37,000 g/mol).

15

Example 7

- 20 Example 1 was repeated, but using a pure polypropylene glycol bismaleamide (MW = 2000) in an amount of 30.00 g (0.150 mol) being used in place of the reaction product of poly(EO-block-PO)amine with maleic anhydride.

Solids content of the end product: 41.3% by weight

- 25 Weight average molecular weight: 36,400 g/mol

Examples 8 to 10

- 30 In Examples 8, 9 and 10, the following components to combat introduction of air were used (otherwise as in Example 1):

- 35 Example 8: 0.010 mol of polydimethylsiloxane bis-(1-propyl 3-methacrylate) (MW = 1100)

Example 9: 0.350 mol of di-n-butyl maleate

Example 10: 0.0075 mol of polydimethylsiloxane bis-
(dipropyleneaminomaleamide)
(MW 5400)

5 In the Use Examples 1 and 2 described below, copolymers from Examples 1 to 10 according to the invention were compared with the known concrete additives of Comparative Examples 1 to 3.

10 Example 11

The following were placed in a 500 ml double-walled reaction vessel:

15 24.2 g of methylpolyethylene glycol 1100 monovinyl ether (0.022 mol), made inert with N₂ and heated to 85°C.

The following were added as three separate feed streams over a period of 120 minutes:

1. 25.48 g (0.26 mol) of maleic anhydride dissolved in 217.8 g (0.198 mol) of methylpolyethylene glycol 1100 monovinyl ether plus 2.68 g (0.01 mol)
25 of dibutyl maleate (temperature of the feed stream: 50°C)
2. 36.72 g (0.51 mol) of acrylic acid
3. 6.14 g of azobisisobutyronitrile in 50 ml of acetone

30

After the addition was complete, the mixture was allowed to react further for 2 hours while simultaneously removing the acetone.

35 The product (brown) was diluted with an equal amount (about 307 g) of water and neutralized to pH 7.0 using 20% strength aqueous sodium hydroxide.

- Solids content of the end product: 38.0% by weight
- Molecular weight (weight average): 30,200 g/mol
- Appearance: turbid, brown

5 Comparative Example 1

Commercial concrete fluidizer "Melment L 10" based on a sulfonated melamine-formaldehyde polycondensate.

10 Comparative Example 2

Maleic monoester-styrene copolymer having the trade name POZZOLITH 330 N.

15 Comparative Example 3

Example 1 of DE 195 13 126 A1 was replicated and the product obtained was employed as a comparison.

20 The aqueous copolymer compositions of the invention and the compositions from the three comparative examples were compared as fluidizers in tests carried out on cement-containing suspensions.

25 These tests demonstrated the excellent processing properties (slump loss method) of the group of aqueous products according to the invention in a transport concrete formulation, while their tendency to achieve very high early strengths as a result of an extremely
30 high reduction in the water:cement ratio is demonstrated in a formulation for producing finished concrete parts.

Use Example 1 (Transport concrete production)

35

In accordance with the appropriate standard, 4.5 kg of Portland cement (CEM I 42.5 R Kiefersfelden) were mixed with 33.0 kg of aggregates (particle size from 0 to

32 mm) and 2.7 kg of water (including the water from the additive) in a cement mixer.

5 The aqueous solutions of the products according to the invention or the comparative products were added and the slump was determined in accordance with DIN 1048 (duplicate determination) after 10 and 40 minutes after addition of the additive.

10 Subsequent to the measurements of the slump after 10 minutes, test specimens having an edge length of 15 x 15 x 15 cm were produced and the compressive strength after 24 hours and the proportion of air pores (from the bulk density of the cured test specimens)
15 were determined.

The results are shown in Table 1:

Table 1: Transport concrete test results

20

Additive	Solids [% w/w]	Amount ¹⁾ [% w/w]	Slump in cm after		Air [% w/w]	24 h comp. strength [MPa]
			10 min.	40 min.		
Ex. 1	41.6	0.20	67.00	58.50	2.1	14.4
Ex. 2	42.0	0.25	65.50	59.00	2.4	14.8
Ex. 3	43.0	0.20	63.25	56.50	1.9	15.0
Ex. 4	42.7	0.20	62.75	57.00	2.3	14.0
Ex. 5	43.7	0.20	65.00	56.00	2.6	14.2
Ex. 6	42.0	0.20	62.75	55.75	2.9	15.3
Ex. 7	41.3	0.20	67.25	57.00	1.7	14.9
Ex. 8	41.5	0.20	65.75	56.25	1.4	15.1
Ex. 9	42.3	0.20	67.75	60.00	3.0	14.0
Ex. 10	42.0	0.20	66.50	59.00	1.3	15.2
Comp.Ex.1	45.3	0.58	57.25	41.00	1.6	15.0
Comp.Ex.2	34.9	0.25	53.75	44.75	2.5	13.7
Comp.Ex.3	37.0	0.25	58.50	48.50	1.9	11.3

- 1) Polymer solids based on the weight of cement
280 kg of CEM I/m³ of concrete

Use Example 2 (Formulation for finished concrete parts)

5

The tests were carried out as described in Use
Example 1, but using 5.75 kg of cement, 2.3 kg of water
(including water from the additive) and 33.0 kg of
aggregate having a slightly altered particle size
distribution.

10

The results are shown in Table 2:

Table 2: Test results for selected products in concrete
for finished parts

15

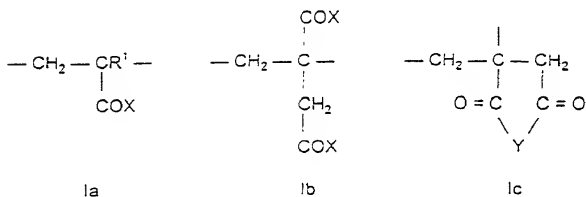
Additive	Solids [% w/w]	Amount ¹⁾ [% w/w]	Slump in cm after		Air [% w/w]	24 h comp. strength [MPa]
			10 min.	40 min.		
Ex. 1	41.6	0.30	56.50	53.25	1.8	39.6
Ex. 2	42.0	0.24	60.75	56.50	1.4	40.4
Ex. 3	43.0	0.30	59.25	55.00	1.9	38.9
Ex. 6	42.3	0.30	56.75	54.75	2.4	40.1
Ex. 7	41.3	0.30	60.00	54.25	1.3	39.9
Comp.Ex.1	45.3	0.92	37.50	-	1.4	38.7
Comp.Ex.2	34.9	0.30	48.50	40.00	1.9	34.6
Comp.Ex.3	37.0	0.30	49.75	43.25	1.7	19.4

- 1) Polymer solids based on the weight of cement
350 kg of CEM I/m³ of concrete

Claims

1. Copolymer based on radicals of unsaturated monocarboxylic or dicarboxylic acid derivatives and oxyalkylene glycol alkenyl ethers, characterized in that they comprise

a) from 51 to 95 mol% of structural units of the formula Ia and/or Ib and/or Ic



where R^1 = hydrogen or an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms,

$X = O_aM, -O-(C_mH_{2m}O)_n-R^2, -NH-(C_mH_{2m}O)_n-R^2,$

$M =$ hydrogen, a monovalent or divalent metal cation, an ammonium ion or an organic amine radical,

$a = \frac{1}{2}$ or 1,

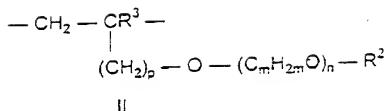
$R^2 =$ hydrogen, an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, a substituted or unsubstituted aryl radical having from 6 to 14 carbon atoms,

$Y = O, NR^2,$

$m = 2$ to 4 and

$n = 0$ to 200,

b) from 1 to 48.9 mol% of structural units of the general formula II



where

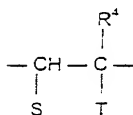
5 R^3 is hydrogen or an aliphatic hydrocarbon radical having from 1 to 5 carbon atoms,

p is from 0 to 3

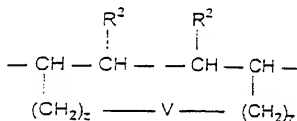
and R^2 , m and n are as defined above,

10

c) from 0.1 to 5 mol% of structural units of the formula IIIa or IIIb



IIIa



IIIb

15

where

$\text{S} = \text{H}, -\text{COO}_a\text{M}, -\text{COOR}^5,$

$\text{T} = -\text{U}^1-(\text{CH}-\text{CH}_2-\text{O})_x-(\text{CH}_2-\text{CH}_2\text{O})_y-\text{R}^6$



20

$-\text{W}-\text{R}^7$

$-\text{CO}-[\text{NH}-(\text{CH}_2)_3]_s-\text{W}-\text{R}^7$

$-\text{CO}-\text{O}-(\text{CH}_2)_z-\text{W}-\text{R}^7$

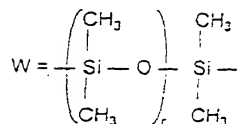
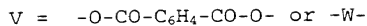
$-(\text{CH}_2)_z-\text{V}-(\text{CH}_2)_z-\text{CH}=\text{CH}-\text{R}^2$

25

$-\text{COOR}^5$ in the case of $\text{S} = -\text{COOR}^5$ or COO_aM

$\text{U}^1 = -\text{CO}-\text{NH}-, -\text{O}-, -\text{CH}_2\text{O}-$

$\text{U}^2 = -\text{NH}-\text{CO}-, -\text{O}-, -\text{OCH}_2-$

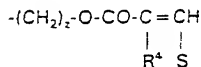
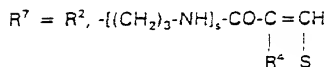
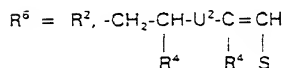


5

 $R^4 = \text{H, CH}_3,$

10

$R^5 =$ an aliphatic hydrocarbon radical having from 3 to 20 carbon atoms, a cycloaliphatic hydrocarbon radical having from 5 to 8 carbon atoms, an aryl radical having from 6 to 14 carbon atoms,



15

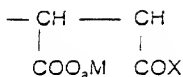
 $r = 2 \text{ to } 100$
 $s = 1, 2$
 $z = 0 \text{ to } 4$
 $x = 1 \text{ to } 150$
 $y = 0 \text{ to } 15$

20

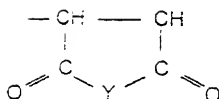
and

d) from 0 to 47.9 mol [lacuna] of structural units of the general formula IVa and/or IVb

25



IVa



IVb

where a, M, X and Y are as defined above.

- 5 2. Copolymer according to claim 1, characterized in that R^1 is a methyl radical.
3. Copolymer according to claim 1 or 2, characterized in that M is a monovalent or divalent metal cation selected from the group consisting of sodium, potassium, calcium and magnesium ions.
- 10 4. Copolymer according to any of claims 1 to 3, characterized in that when R^2 = phenyl, the phenyl radical is substituted by one or more hydroxyl, carboxyl or sulfonic acid groups.
- 15 5. Copolymer according to any of claims 1 to 4, characterized in that, in the formula II, $p = 0$ and $m = 2$.
- 20 6. Copolymer according to any of claims 1 to 5, characterized in that it comprises from 55 to 75 mol% of structural units of the formula Ia and/or Ib and/or Ic, from 19.5 to 39.5 mol% of structural units of the formula II, from 0.5 to 2 mol% of structural units of the formula IIIa and/or IIIb and from 5 to 20 mol% of structural units of the formula IVa and/or IVb.
- 25 7. Copolymer according to any of claims 1 to 6, characterized in that it further comprises up to 50 mol%, in particular up to 20 mol%, based on the sum of the structural units of the formulae I, II,
- 30

III and IV, of structural units whose monomer is a vinyl or (meth)acrylic acid derivative.

8. Copolymer according to claim 7, characterized in that the additional structural units are formed from a monomeric vinyl derivative styrene, α -methylstyrene, vinyl acetate, vinyl propionate, ethylene, propylene, isobutene, n-vinylpyrrolidone, allylsulfonic acid, methallylsulfonic acid, vinylsulfonic acid or vinylphosphonic acid.
9. Copolymer according to claim 7, characterized in that the additional structural units are formed from a monomeric (meth)acrylic acid derivative hydroxyalkyl (meth)acrylate, acrylamide, methacrylamide, AMPS, methyl methacrylate, methyl acrylate, butyl acrylate or cyclohexyl acrylate.
10. Copolymer according to any of claims 1 to 9, characterized in that it has a mean molecular weight of from 1000 to 100,000 g/mol.
11. Process for preparing a copolymer according to any of claims 1 to 10, characterized in that from 51 to 95 mol% of an unsaturated monocarboxylic or dicarboxylic acid derivative, from 1 to 48.9 mol% of an oxyalkylene glycol alkenyl ether, from 0.1 to 5 mol% of a vinylic polyalkylene glycol, polysiloxane or ester compound and from 0 to 55 mol% of a dicarboxylic acid derivative are polymerized with the aid of a free-radical initiator.
12. Process according to claim 11, characterized in that from 55 to 75 mol% of an unsaturated monocarboxylic or dicarboxylic acid derivative, from 19.5 to 39.5 mol% of an oxyalkylene glycol alkenyl ether, from 0.5 to 2 mol% of a vinylic

polyalkylene glycol, polysiloxane or ester compound and from 5 to 20 mol% of a dicarboxylic acid derivative are used.

- 5 13. Process according to claim 11 or 12, characterized
in that up to 50 mol%, in particular up to
20 mol%, based on the monomers comprising the
structural units of the formulae I, II, III and
10 IV, of a vinyl or (meth)acrylic acid derivative
are additionally copolymerized.
14. Process according to any of claims 11 to 13,
characterized in that the polymerization is
carried out in aqueous solution at a temperature
15 of from 20 to 100°C.
15. Process according to claim 14, characterized in
that the concentration of the aqueous solution is
from 30 to 50% by weight.
20
16. Process according to any of claims 11 to 13,
characterized in that the polymerization is
carried out without solvents with the aid of a
free-radical initiator at temperatures of from 20
25 to 150°C.
17. Use of a copolymer according to any of claims 1
to 10 as an additive to aqueous suspensions based
on mineral or bituminous binders, in particular
30 cement, plaster of Paris, lime, anhydrite or other
binders based on calcium sulfate or binders based
on pulverulent dispersion binders.
18. Use of a copolymer as claimed in claim 17,
characterized in that it is used in an amount of
from 0.01 to 10% by weight, preferably from 0.1 to
35 5% by weight, based on the weight of the mineral
binder.

PTO/SB/01 (4-96)

Approved for use through 9/30/98

OMB 0651-0032

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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☐ Declaration Submitted after Initial Filing

Attorney Docket Number

First Named Inventor

COMPLETE IF KNOWN

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

(Title of the invention)

the specification of which

☐ is attached hereto
OR

☒ was filed on (MM/DD/YYYY)

March 14, 2000

as United States Application Number or PCT International

Application Number

PCT/EP00/0225

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
199 26 611.5	DE	June 11, 99	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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U.S. Parent Application or PCT Parent
NumberParent Filing Date
(MM/DD/YYYY)Parent Patent Number
(if applicable)☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

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Name of Sole or First Inventor:

☐ A petition has been filed for this unsigned inventor

Given Name (first and middle (if any))

Family Name or Surname

Gerhard

ALBRECHT

Inventor's
Signature

Gerhard Albrecht

Date

04/24/01

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☒ Additional inventors are being named on the supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

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DECLARATION

ADDITIONAL INVENTOR(S)
Supplemental Sheet

Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Christian	Middle Initial		Family Name	HÜBSCH	Suffix	
Inventor's Signature	<i>Ch. Hübsch</i>				Date	25.04.01	
Residence: City	83703 Gmund	State		Country	Germany	Citizenship	DE
Post Office Address	Dorfstraße 14, 83703 Gmund, Germany						
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Hubert	Middle Initial		Family Name	LEITNER	Suffix	
Inventor's Signature	<i>Hubert Leitner</i>				Date	2001-05-09	
Residence: City	8967 Haus/Ennstal	State		Country	Austria	Citizenship	AT
Post Office Address	Oberhauser Straße 149, 8967 Haus/Ennstal, Austria						
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Harald	Middle Initial		Family Name	GRASSL	Suffix	
Inventor's Signature	<i>Harald Grassl</i>				Date	04/26/01	
Residence: City	83471 Schöna	State		Country	Germany	Citizenship	DE
Post Office Address	Untersteiner Straße 18, 83471 Schöna, Germany						
Post Office Address							
City		State		Zip		Country	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Alfred	Middle Initial		Family Name	KERN	Suffix	
Inventor's Signature	<i>Alfred Kern</i>				Date	04/27/01	
Residence: City	84558 Kirchweidach	State		Country	Germany	Citizenship	DE
Post Office Address	Ringstraße 24, 84558 Kirchweidach, Germany						
Post Office Address							
City		State		Zip		Country	
<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto							

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